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(54) SOFT MAGNETIC MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a soft magnetic material which does not contain lead, has high water resistance and is composed of soft magnetic metals and a glass composite having better wettability, with the soft magnetic metals at around molding-body firing temperature. SOLUTION: This soft magnetic material is provided by covering the powder surface of the soft magnetic metals with a phosphate glass composite composed of, substantially in mole indication, P<sub>2</sub>O<sub>5</sub> 39-47%, Al<sub>2</sub>O<sub>3</sub> 3-6%, ZnO 8-12%, BaO 1-12%, Li<sub>2</sub>O 7-17%, Na<sub>2</sub>O 7-17%, and K<sub>2</sub>O 0-8%, where ZnO+BaO is 19-24%, and Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>O is 25-33%.

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## CLAIMS

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[Claim(s)]

[Claim 1] Substantially the particulate matter front face of a soft magnetism metal by mol display P2 O539-47%, aluminum 2O3 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, Li2 O 7 - 17%, Na2 O 7 - 17%, K2 O Soft magnetic materials which have covered 0 - 8%, however ZnO+BaO with the phosphate glass constituent with which Li2 O+Na2 O+K2 O consists of 25 - 33% 19 to 24%.

[Claim 2] It is P2 O5 by mol display to a soft magnetism metal and a real target. 39 - 47%, aluminum 2O3 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, Li2 O 7 - 17%, and Na2 O 7 - 17%, and K2 O 0 - 8%, however ZnO+BaO -- 19 - 24%, and 2O25 - 33% of Li2 O+Na2 O+K from -- soft magnetic materials which have mixed the becoming phosphate glass constituent.

[Claim 3] It is P2 O5 by mol display to a soft magnetism metal and a real target. 39 - 47%, aluminum 2O3 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, Li2 O 7 - 17%, and Na2 O 7 - 17%, and K2 O 0 - 8%, however ZnO+BaO -- 19 - 24%, and 2O25 - 33% of Li2 O+Na2 O+K from -- soft magnetic materials which have carried out sinter molding of the becoming phosphate glass constituent.

[Claim 4] Said soft magnetism metal A Fe-Si-B-M (at least one sort of elements with which M was chosen from Cr, W, Mo, and Nb) system amorphous alloy, A Co-Fe-Si-B system amorphous alloy, Fe-Cu-Si-B-M (at least one sort of elements with which M was chosen from Nb, W, Ta, Zr, Hf, Ti, and Mo) system nano crystal, Soft magnetic materials according to claim 1, 2, or 3 which are what consists of Sendust, a permalloy, a Fe-Si system alloy, a Fe-nickel system alloy, or the pure iron.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the soft magnetic materials which consist of a soft magnetism metal and a glass constituent.

[0002]

[Description of the Prior Art] As soft magnetic materials, since amorphous soft magnetism metals, such as for example, a Fe-Si-B-M (at least one sort of elements with which M was chosen from Cr, W, Mo, and Nb) system amorphous alloy, and a Co-Fe-Si-B system amorphous alloy, are excellent in corrosion resistance, abrasion resistance, reinforcement, permeability, etc. compared with a crystal ingredient, they are used as a choke coil, a core iron material of a flyback transformer, etc. However, since it is necessary to make electric insulation have while in the case of said soft magnetism metal maintaining an amorphous state so that the soft magnetism may not be spoiled, if it is line trap \*\*\*\*\* about pressing in the binding material of electric insulation below temperature lower than the crystallization temperature and about 500 degrees C, there is nothing. Then, pressing in temperature lower than the crystallization temperature of said soft magnetism metal is performed by generally mixing and heating the binding material which becomes the particulate matter of said soft magnetism metal from a glass constituent with softening temperature lower than the crystallization temperature. That is, since said binding material constituted some Plastic solids as a binding material between the particulate matters of said soft magnetism metal, properties, like there are little electric insulation in a room temperature and reactivity with said soft magnetism metal were made indispensable so that not only a low-temperature softening degree but the resistance by application of pressure or heating and the soft magnetism of said soft magnetism metal might not be spoiled, and the glass constituent which uses PbO as a principal component was conventionally used as said binding material.

[0003]

[Problem(s) to be Solved by the Invention] However, since the glass constituent which uses PbO as a principal component contained lead harmful to an environment, it had a problem from the point of an environmental cure. Moreover, in the case of the glass constituent of the system which does not contain lead, when the water resisting property was low, a content heavy metal harmful to an environment was eluted, and there was a problem from the point of an environmental cure similarly. Moreover, the demand to a recent years more firm and precise Plastic solid is strong, and, for this reason, what has better wettability with said soft magnetism metal is needed near Plastic solid burning temperature. Therefore, the object of this invention is in the point of offering the soft magnetic materials which consist of glass constituents with more sufficient wettability and soft magnetism metals with a soft magnetism metal, near Plastic solid burning temperature while it is made in view of the above-mentioned actual condition and equipped with a high water resisting property excluding lead.

[0004]

[Means for Solving the Problem] [Configuration] the description configuration of the soft magnetic materials of invention of claim 1 It is the particulate matter front face of a soft magnetism metal by mol display substantially P2 O5 39 - 47%, aluminum 2O3 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, Li2 O 7 - 17%, and Na2 O 7 - 17%, and K2 O 0 - 8%, however ZnO+BaO -- 19 - 24%, and 2O25 - 33% of Li2 O+Na2 O+K from -- it is in the point covered with the becoming phosphate glass constituent.

[0005] The description configuration of the soft magnetic materials of invention of claim 2 is a mol display at a soft magnetism metal and a real target. P2 O5 39 - 47%, aluminum 2O3 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, and Li2 O 7 - 17%, and Na2 O 7 - 17%K 2O0 - 8%, however ZnO+BaO -- 19 - 24%, and 2O25 - 33%

of Li<sub>2</sub>O+Na<sub>2</sub>O+K from -- it is in the point which has mixed the becoming phosphate glass constituent. [0006] The description configuration of the soft magnetic materials of invention of claim 3 is a mol display at a soft magnetism metal and a real target. P<sub>2</sub>O<sub>5</sub> 39 - 47%, aluminum 2O<sub>3</sub> 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, and Li<sub>2</sub>O 7 - 17%, and Na<sub>2</sub>O 7 - 17% K<sub>2</sub>O 0 - 8%, however ZnO+BaO -- 19 - 24%, and 2O<sub>25</sub> - 33% of Li<sub>2</sub>O+Na<sub>2</sub>O+K from -- it is in the point which has carried out sinter molding of the becoming phosphate glass constituent.

[0007] Said soft magnetism metal in the description configuration of the soft magnetic materials which the description configuration of invention of claim 4 requires for above-mentioned claim 1, claim 2, or claim 3 A Fe-Si-B-M (at least one sort of elements with which M was chosen from Cr, W, Mo, and Nb) system amorphous alloy, A Co-Fe-Si-B system amorphous alloy, Fe-Cu-Si-B-M (at least one sort of elements with which M was chosen from Nb, W, Ta, Zr, Hf, Ti, and Mo) system nano crystal, It is in the point which is what consists of Sendust, a permalloy, a Fe-Si system alloy, a Fe-nickel system alloy, or the pure iron.

[0008] [An operation and effectiveness] In the description configuration of claims 1-4 of this invention especially substantially by mol display P<sub>2</sub>O<sub>5</sub> 39 - 47%, aluminum 2O<sub>3</sub> 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, Li<sub>2</sub>O 7 - 17%, Na<sub>2</sub>O 7 - 17%, K<sub>2</sub>O 0 - 8%, however ZnO+BaO -- 19 - 24%, and 2O<sub>25</sub> - 33% of Li<sub>2</sub>O+Na<sub>2</sub>O+K from -- the operation and effectiveness by the becoming phosphate glass constituent are explained.

[0009] P<sub>2</sub>O<sub>5</sub> It is the optimal glass network former for low-melting-glass production which does not contain PbO. P<sub>2</sub>O<sub>5</sub> since a possibility that the devitrification nature of glass may deposit a crystal during increase and Plastic solid baking with a metal, and may make a firm Plastic solid acquisition impossible etc. will arise if there are too few contents -- more than 39 mol % -- it is necessary to make it contain However, since moisture content will also increase inevitably and a water resisting property will fall extremely if there are too many contents, as for the content, less than [ 47 mol % ] is desirable.

[0010] aluminum 2O<sub>3</sub> It is a component effective in a water resisting property. Moreover, little aluminum 2O<sub>3</sub> In phosphate glass, it works to the consolidation of the glass network structure, and the stability over devitrification of glass is increased. then -- for raising a water resisting property -- more than 3 mol % -- it is necessary to make it contain However, if there are too many contents, since the viscosity of glass will increase and a low-temperature softening degree will be spoiled, as for the content, less than [ 6 mol % ] is desirable.

[0011] Since ZnO raises a water resisting property, without seldom spoiling low-melting, it is a component indispensable to the low-melt point glass which does not contain PbO. However, if a content increases too much, wettability with a metal will be checked and the devitrification inclination of glass will also increase. Moreover, the presentation which are is not desirable from the point of an environmental cure. Therefore, 8-22-mol % of a content is suitable. Since BaO has the same operation effectiveness as ZnO, it is a component effective in a permutation with ZnO. However, since the effectiveness which prevents low-melting and wettability from ZnO is large, the direction of a content which is not is good. Therefore, 1-12-mol % of a content is suitable. And 19-24-mol% of the sum total content of ZnO and BaO is suitable.

[0012] Li<sub>2</sub>O, Na<sub>2</sub>O, and K<sub>2</sub>O are components effective for an improvement of the melting nature of glass, and physical properties. However, if a content increases too much, although promoted, since the water resisting property of glass deteriorates, it is not desirable [ low-melting ]. About Li<sub>2</sub> from low-melting and water resisting property O, and Na<sub>2</sub>O, 7-17-mol % of a content is respectively desirable. Since the effectiveness of degrading a water resisting property is the largest, 0-8-mol % of a content is suitable for K<sub>2</sub>O. Moreover, since the way made to live together two or more sorts can control waterproof degradation according to a mixed alkali effect, 25-33-mol % of a content is suitable for an alkali-metal oxide as the total quantity of Li<sub>2</sub>O, Na<sub>2</sub>O, and K<sub>2</sub>O.

[0013] Therefore, since Plastic solid baking could be performed at low temperature, and the electromagnetic properties of the produced Plastic solid were not spoiled and also it has the high water resisting property by constituting soft magnetic materials from a soft magnetism metal and an above-mentioned phosphate glass constituent, excluding lead at all, it is desirable also from the point of an environmental cure. Furthermore, since the wettability of a soft magnetism metal and a glass constituent is good near Plastic solid burning temperature, a firmer and precise Plastic solid is acquired.

[0014] And since the particulate matter front face of a soft magnetism metal is covered with said phosphate glass constituent according to the description configuration of the soft magnetic materials concerning invention according to claim 1, and the glass constituent softened with heating at the time of Plastic solid

baking enters between the particulate matters of said soft magnetism metal at homogeneity, much more above-mentioned effectiveness is puffed up. According to the description configuration of the soft magnetic materials concerning invention according to claim 2, since what is necessary is just to mix said phosphate glass constituent with said soft magnetism metal, above-mentioned effectiveness can be acquired simple. According to the description configuration of the soft magnetic materials concerning invention according to claim 3, since sinter molding of said soft magnetism metal and said phosphate glass constituent is carried out beforehand, the Plastic solid which consists of uniform mixture by the time of calcinating a Plastic solid eventually is acquired, and above-mentioned effectiveness can be acquired certainly. According to the description configuration of the soft magnetic materials concerning invention according to claim 4, in various soft magnetism metals, the effectiveness of claims 1-3 can be acquired and it is convenience.

[0015]

[Embodiment of the Invention] The gestalt of operation of this invention is explained briefly below. The particulate matter and phosphate glass constituent particulate matter (mean particle diameter of about 3 micrometers) of a soft magnetism metal of Fe78Si nine B13 (mean particle diameter of about 65 micrometers) were prepared to the mixing ratio (volume ratio) of 95:5, and the soft magnetic materials which consist of composite powder grain which covered the particulate matter front face of a soft magnetism metal with glass powder grain were produced using the particulate matter surface treatment equipment shown in drawing 1 as follows. Drawing 1 shows the flank sectional view (drawing cut towards intersecting perpendicularly with an axial center in the location near the piece side edge section of a cylindrical cup 1) of particulate matter surface treatment equipment. Supply the particulate matter 9 prepared inside the cylindrical cup 1 which can be sealed, and a particulate matter 9 is pressed and compressed by the press member 5 attached at the head of the 1st arm 4 which projects radially by the boss 3 fixed to the revolving shaft 2. The actuation which scratches a particulate matter 9 by SUKUREPA 7 attached at the head of the 1st arm and the 2nd crossing arm 6 which projects radially from the boss 3 is repeated by revolution actuation of the 1st arm 4 and the 2nd arm 6. Surface fusion was made to induce between particulate matters according to powerful sticking-by-pressure frictional force, and the soft magnetic materials which made the particulate matter front face of a soft magnetism metal cover with glass powder grain were produced.

[0016] Next, the example of a phosphate glass constituent is explained to a detail. The phosphate glass constituent was produced as follows. After often mixing the raw material of carbonates (for example, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, etc.), oxides (for example, BaO, ZnO, etc.), hydroxides (for example, aluminum<sub>3</sub>(OH) etc.), and acids (for example, H<sub>3</sub>PO<sub>4</sub> etc.), 900 degrees C was fused for 1 hour using the crucible of the quality of a high alumina, stirring intermittently. On the stainless plate currently heated beforehand, it is begun to pass melt and it is annealed. Substantially then, by mol display P2 O<sub>5</sub> 39 - 47%, aluminum 2O<sub>3</sub> 3 - 6%, ZnO 8 - 22%, BaO 1 - 12%, and Li<sub>2</sub>O 7 - 17%, and Na<sub>2</sub>O 7 - 17%, and K<sub>2</sub>O 0 - 8%, however ZnO+BaO - 19 - 24%, and 2O<sub>25</sub> - 33% of Li<sub>2</sub>O+Na<sub>2</sub>O+K from -- the phosphate glass constituent of the becoming presentation was obtained. Thus, the glass transition point of the produced phosphate glass constituent, the water resisting property, and the wetting angle were measured.

[0017] The glass transition point was measured on the temperature-up conditions of 10 degrees C / min by the DSC method. This value shows low-melting [ of a glass constituent ].

[0018] A water resisting property shows the value (W) calculated as follows. 5g of glass constituents was made immersed for 60 minutes into 500ml of pure water, and W was calculated by the degree type from the weight (g<sub>80</sub>) at the time of making it dry at 80 degrees C the weight (g<sub>0</sub>) when pulling up, and after that for 24 hours.

A water resisting property is so good that W=(g<sub>0</sub>-g<sub>80</sub>)/g<sub>80</sub>×100, therefore the value of W are small, and 2% or less of W is desirable from an activity.

[0019] Next, the wetting angle was measured as follows. In addition, as it is indicated in drawing 2 as a wetting angle, it is the thing of the include angle theta of the solid phase-liquid phase interface of a drop, and a liquid phase-gaseous-phase interface, and it is shown that the wettability in which a liquid soaks a solid-state front face is high, so that wetting angle theta is small. First, the cylinder which hardened and created the glass constituent is carried on the ribbon of an amorphous metal, it puts into a 460-degree C furnace, and they are after 30-minute maintenance and the wetting angle theta 460. It measured. It is the 540-degree C wetting angle theta 540 to raising and this appearance about temperature after that. It measured. And it is theta 460 in order for wettability with a soft magnetism metal to obtain a better glass constituent near Plastic

solid burning temperature, 100 degrees C or less, and the ratio theta 540 of a wetting angle / theta 460 What is about 0.4 or less is desirable.

[0020] The presentation and each property are shown in tables 1 and 2 about the examples 6-9 of a comparison as an example of the glass constituent of the presentation which is not included in this invention about examples 1-5 as an example of a phosphate glass constituent.

[0021]

[A table 1]

| (数字はモル%)   | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|--|------|------|------|------|------|------|------|------|------|
| P <sub>2</sub> O <sub>5</sub>                            | 41.7 | 45.5 | 43.5 | 40.5 | 46.5 | 44.0 | 50.0 | 43.5 | 33.0 |
| Al <sub>2</sub> O <sub>3</sub>                           | 4.8  | 4.8  | 5.0  | 5.0  | 4.7  | 5.0  | 4.4  | 5.0  | 5.9  |
| ZnO  | 18.6 | 11.1 | 20.5 | 21.5 | 10.8 | 22.0 | 20.0 | 8.5  | 26.7 |
| BaO  | 3.0  | 10.6 | 2.0  | 2.0  | 10.4 |      |      | 14.0 |      |
| ZnO + BaO  | 21.6 | 21.7 | 22.5 | 23.5 | 21.2 | 21.5 | 20.0 | 22.5 | 26.7 |
| Li <sub>2</sub> O  | 16.0 | 14.0 | 7.5  | 15.5 | 13.7 | 4.0  | 12.8 | 14.5 | 17.2 |
| Na <sub>2</sub> O  | 16.0 | 14.0 | 14.5 | 15.5 | 13.7 | 14.5 | 12.8 | 14.5 | 17.2 |
| K <sub>2</sub> O   |      |      | 7.0  |      |      | 10.5 |      |      |      |
| Li <sub>2</sub> O + Na <sub>2</sub> O + K <sub>2</sub> O | 32.0 | 28.0 | 29.0 | 31.0 | 27.4 | 29.0 | 25.6 | 23.0 | 31.4 |

[0022]

[A table 2]

|                                     | 1                | 2    | 3    | 4    | 5    | 6    | 7     | 8    | 9    |
|-------------------------------------|------------------|------|------|------|------|------|-------|------|------|
| T <sub>g</sub> (°C)                 | 303              | 311  | 307  | 312  | 313  | 315  | 299   | 315  | 330  |
| 耐水性 (%)                             | 1.38             | 1.63 | 1.93 | 1.38 | 1.75 | 4.04 | 36.63 | 1.07 | —    |
| 濡れ角                                 | θ <sub>460</sub> | 92°  | 100° | 84°  | 98°  | 92°  | 129   | 103  | 97   |
|                                     | θ <sub>540</sub> | 18°  | 29°  | 11°  | 28°  | 34°  | 16    | 59   | 103  |
| θ <sub>540</sub> / θ <sub>460</sub> |                  | 0.20 | 0.29 | 0.13 | 0.29 | 0.37 | 0.12  | 0.57 | 1.06 |

※ 結晶析出のため測定不能

[0023] As shown in tables 1 and 2, unlike the glass constituent of the conventional presentation, the phosphate glass constituent of the presentation which requires the examples 6-9 of a comparison for this invention to that of low melting nature, a water resisting property, and \*\*\*\*\* that lacks in at least one property among wettability is equipped with low melting nature, the water resisting property, and the property that was excellent about wettability all.

[0024] [Another operation gestalt] Other operation gestalten are explained below.

\*\*1\*\* The approach of covering the particulate matter front face of a soft magnetism metal with a glass constituent may be covered with the approach not only by a previous operation gestalt but a sol gel process or the plasma method etc.

\*\*2\*\* What mixed the glass constituent with the soft magnetism metal not only by the previous operation gestalt but by the mixer etc. is sufficient as soft magnetic materials.

\*\*3\*\* What carried out sinter molding of what [ what carried out sinter molding of not only a previous operation gestalt but a soft magnetism metal and the glass constituent ], for example, those composite powder grain, mixture, etc., is sufficient as soft magnetic materials.

\*\*4\*\* Don't restrict to the component explained in the previous example, and a phosphate glass constituent is aluminum 2O3. P2 O5 They are B-2 O3 and La 2O3 about small quantity. And TiO2 You may permute and the small quantity of ZnO or BaO may be permuted by SrO, CaO, MgO, etc.

\*\*5\*\* A soft magnetism metal is not what is restricted to Fe78Si nine B13 explained with the previous operation gestalt. For example, the Fe-Si-B-M (at least one sort of elements with which M was chosen from Cr, W, Mo, and Nb) system amorphous alloy which consists of other presentation ratios, Nano crystal, such as a Co-Fe-Si-B system amorphous alloy and a Fe-Cu-Si-B-M (at least one sort of elements with which M was chosen from Nb, W, Ta, Zr, Hf, Ti, and Mo) system, You may be Sendust, various permalloys, a Fe-Si system alloy, a Fe-nickel system alloy, or pure iron.

\*\*6\*\* although especially the content of the phosphate glass constituent in soft magnetic materials is not limited, in order to achieve the function as a binding material -- about 0.5 -- an about [-20vol%] content is desirable.

\*\*7\*\* When covering the particulate matter front face of a soft magnetism metal with a phosphate glass

constituent, in order for the chip omission of the glass constituent etc. to protect that the thickness becomes an ununiformity, it is about 3 micrometers. A coat by the following thickness is desirable.

\*\*8\*\* The glass constituent which constitutes the soft magnetic materials concerning this invention may contain the unescapable impurity. In addition, it is better for the glass constituent of the system containing Sn oxides, such as SnO, to have a problem in respect of electric insulation etc., since Metal Sn deposits, and not to contain Sn oxide.

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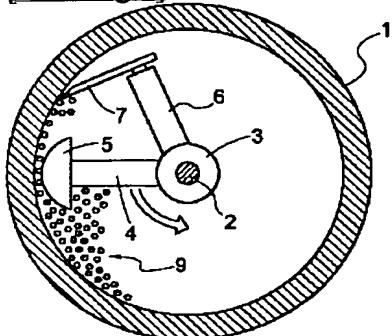
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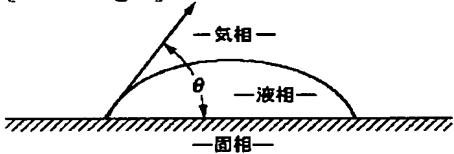
DRAWINGS

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[Drawing 1]



[Drawing 2]



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[Translation done.]

(19)日本国特許庁 (JP)

## (12) 公開特許公報 (A)

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|--------------------------|------------------------------------|---------------|---------------------------|
| H 0 1 F 1/20             |                                    | H 0 1 F 1/20  | 4 G 0 6 2                 |
| B 2 2 F 1/02             |                                    | B 2 2 F 1/02  | E 4 K 0 1 8               |
| C 0 3 C 3/17             |                                    | C 0 3 C 3/17  | 5 E 0 4 1                 |
| 8/08                     |                                    | 8/08          |                           |
| C 2 2 C 33/02            |                                    | C 2 2 C 33/02 | L                         |
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最終頁に続く

(54)【発明の名称】軟磁性材料

## (57)【要約】

【課題】鉛を含まず、高い耐水性を備えると共に、成形体焼成温度付近で軟磁性金属との濡れ性がより良いガラス組成物と、軟磁性金属とから構成される軟磁性材料を提供する。

【解決手段】軟磁性金属の粉粒体表面を、実質的にモル表示で、 $P_2O_5$  3.9~4.7%、 $Al_2O_3$  3~6%、 $ZnO$  8~22%、 $BaO$  1~12%、 $Li_2O$  7~17%、 $Na_2O$  7~17%、 $K_2O$  0~8%、ただし、 $ZnO + BaO$  が19~24%、 $Li_2O + Na_2O + K_2O$  が25~33%からなるリン酸塩ガラス組成物により被覆してある軟磁性材料。

結晶化温度よりも低い温度での加圧成形が行われている。つまり、前記結合材は前記軟磁性金属の粉粒体間の結合材として成形体の一部を構成するので、低温軟化性だけでなく、加圧又は加熱による耐性、前記軟磁性金属の軟磁性を損なわないように室温での電気絶縁性、及び前記軟磁性金属との反応性が少ない等の性質が不可欠とされ、従来は、PbOを主成分とするガラス組成物が、前記結合材として用いられていた。

## 【0003】

- 10 【発明が解決しようとする課題】しかしながら、PbOを主成分とするガラス組成物は、環境に有害な鉛を含有するため、環境対策の点から問題があった。また、鉛を含有しない系のガラス組成物の場合でも、耐水性が低いと、環境に有害な含有重金属が溶出し、同様に環境対策の点から問題があった。また、近年、より強固で緻密な成形体に対する要求が強く、このため成形体焼成温度付近で前記軟磁性金属との濡れ性がより良いものが必要となってきた。従って、本発明の目的は、上記実情に鑑みてなされたものであって、鉛を含まず、高い耐水性20を備えると共に、成形体焼成温度付近で軟磁性金属との濡れ性がより良いガラス組成物と、軟磁性金属とから構成される軟磁性材料を提供する点にある。

## 【0004】

- 【課題を解決するための手段】【構成】請求項1の発明の軟磁性材料の特徴構成は、軟磁性金属の粉粒体表面を、実質的にモル表示で、P<sub>2</sub>O<sub>5</sub> 39～47%、Al<sub>2</sub>O<sub>3</sub> 3～6%、ZnO 8～22%、BaO 1～12%、Li<sub>2</sub>O 7～17%、Na<sub>2</sub>O 7～17%、K<sub>2</sub>O 0～8%、ただし、ZnO+BaOが19～24%、Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>Oが25～33%からなるリン酸塩ガラス組成物により被覆してある軟磁性材料。
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【発明の詳細な説明】  
【0001】  
【発明の属する技術分野】本発明は、軟磁性金属及びガラス組成物から構成される軟磁性材料に関する。  
【0002】  
【従来の技術】軟磁性材料として、例えば、Fe-Si-B-M(MはCr, W, Mo, Nbから選ばれた少なくとも1種の元素)系非晶質合金、Co-Fe-Si-B系非晶質合金、Fe-Cu-Si-B-M(MはNb, W, Ta, Zr, Hf, Ti及びMoから選ばれた少なくとも1種の元素)系ナノクリスタル、センダスト、ペーマロイ、Fe-Si系合金、Fe-Ni系合金、又は純鉄のうちのいずれかからなるものである請求項1又は請求項2又は請求項3記載の軟磁性材料。

- 40 【0003】請求項2の発明の軟磁性材料の特徴構成は、軟磁性金属、及び、実質的にモル表示で、P<sub>2</sub>O<sub>5</sub> 39～47%、Al<sub>2</sub>O<sub>3</sub> 3～6%、ZnO 8～22%、BaO 1～12%、Li<sub>2</sub>O 7～17%、Na<sub>2</sub>O 7～17%、K<sub>2</sub>O 0～8%、ただし、ZnO+BaOが19～24%、Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>Oが25～33%からなるリン酸塩ガラス組成物を混合してある点にある。
- 【0004】請求項3の発明の軟磁性材料の特徴構成は、軟磁性金属、及び、実質的にモル表示で、P<sub>2</sub>O<sub>5</sub> 39～47%、Al<sub>2</sub>O<sub>3</sub> 3～6%、ZnO 8～22%、BaO 1～12%、Li<sub>2</sub>O 7～17%、Na<sub>2</sub>O 7～17%、K<sub>2</sub>O 0～8%、ただし、ZnO+BaOが19～24%、Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>Oが25～33%からなるリン酸塩ガラス組成物を焼成形してある点にある。

- 50 【0005】請求項4の発明の特徴構成は、上記請求項1又は請求項2又は請求項3に係る軟磁性材料の特徴構

## 【特許請求の範囲】

【請求項1】 軟磁性金属の粉粒体表面を、実質的にモル表示で、P<sub>2</sub>O<sub>5</sub> 39～47%、Al<sub>2</sub>O<sub>3</sub> 3～6%、ZnO 8～22%、BaO 1～12%、Li<sub>2</sub>O 7～17%、Na<sub>2</sub>O 7～17%、K<sub>2</sub>O 0～8%、ただし、ZnO+BaOが19～24%、Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>Oが25～33%からなるリン酸塩ガラス組成物により被覆してある軟磁性材料。

【請求項2】 軟磁性金属、及び、実質的にモル表示で、P<sub>2</sub>O<sub>5</sub> 39～47%、Al<sub>2</sub>O<sub>3</sub> 3～6%、ZnO 8～22%、BaO 1～12%、Li<sub>2</sub>O 7～17%、Na<sub>2</sub>O 7～17%、K<sub>2</sub>O 0～8%、ただし、ZnO+BaOが19～24%、Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>Oが25～33%からなるリン酸塩ガラス組成物を混合してある軟磁性材料。

【請求項3】 軟磁性金属、及び、実質的にモル表示で、P<sub>2</sub>O<sub>5</sub> 39～47%、Al<sub>2</sub>O<sub>3</sub> 3～6%、ZnO 8～22%、BaO 1～12%、Li<sub>2</sub>O 7～17%、Na<sub>2</sub>O 7～17%、K<sub>2</sub>O 0～8%、ただし、ZnO+BaOが19～24%、Li<sub>2</sub>O+Na<sub>2</sub>O+K<sub>2</sub>Oが25～33%からなるリン酸塩ガラス組成物を焼成形してある軟磁性材料。

【請求項4】 前記軟磁性金属は、Fe-Si-B-M(MはCr, W, Mo, Nbから選ばれた少なくとも1種の元素)系非晶質合金、Co-Fe-Si-B系非晶質合金、Fe-Cu-Si-B-M(MはNb, W, Ta, Zr, Hf, Ti及びMoから選ばれた少なくとも1種の元素)系ナノクリスタル、センダスト、ペーマロイ、Fe-Si系合金、Fe-Ni系合金、又は純鉄のうちのいずれかからなるものである請求項1又は請求項2又は請求項3記載の軟磁性材料。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、軟磁性金属及びガラス組成物から構成される軟磁性材料に関する。

## 【0002】

【従来の技術】軟磁性材料として、例えば、Fe-Si-B-M(MはCr, W, Mo, Nbから選ばれた少なくとも1種の元素)系非晶質合金やCo-Fe-Si-B系非晶質合金等の非晶質軟磁性金属が、結晶材料と比べて、耐食性、耐摩耗性、強度、透磁率等に優れることから、チョークコイルやフライバックトランジスタの磁芯材料等として用いられている。しかし、前記軟磁性金属の場合、その軟磁性を損なわないように非晶質状態を維持すると共に、電気絶縁性を備えさせる必要があるので、その結晶化温度よりも低い温度、約500℃以下で、電気絶縁性の結合材と共に加圧成形を行わなければならぬ。そこで、一般に、前記軟磁性金属の粉粒体に、その結晶化温度よりも軟化点の低いガラス組成物からなる結合材を混合し、加熱することにより、前記軟磁性金属の

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成における前記軟磁性金属は、Fe-Si-B-M（MはCr, W, Mo, Nbから選ばれた少なくとも1種の元素）系非晶質合金、Co-Fe-Si-B系非晶質合金、Fe-Cu-Si-B-M（MはNb, W, Ta, Zr, Hf, Ti及びMoから選ばれた少なくとも1種の元素）系ナノクリスタル、センダスト、パーマロイ、Fe-Si系合金、Fe-Ni系合金、又は純鉄のうちのいずれかからなるものである点にある。

【0008】〔作用及び効果〕本発明の請求項1～4の特徴構成において、殊に、実質的にモル表示で、 $P_2O_5$  39～47%、 $Al_2O_3$  3～6%、 $ZnO$  8～22%、 $BaO$  1～12%、 $Li_2O$  7～17%、 $Na_2O$  7～17%、 $K_2O$  0～8%、ただし、 $ZnO + BaO$  が19～24%、 $Li_2O + Na_2O + K_2O$  が25～33% からなるリン酸塩ガラス組成物による作用及び効果について説明する。

【0009】 $P_2O_5$  は、 $PbO$ を含まない低融点ガラス作製には、最適のガラス網目形成成分である。 $P_2O_5$  の含有量が少なすぎるとガラスの失透性が増し、金属との成形体焼成中に結晶を析出して、強固な成形体を得不能にするおそれ等が生ずるので、39モル%以上含有させる必要がある。しかし、含有量が多すぎると必然的に含水量が多くなり、耐水性は極端に低下してしまうので、その含有量は47モル%以下が好ましい。

【0010】 $Al_2O_3$  は、耐水性に有効な成分である。また、少量の $Al_2O_3$  はリン酸塩ガラス中ではガラス網目構造の強化に働き、ガラスの失透に対する安定性を増す。そこで、耐水性を向上させるには、3モル%以上含有させる必要がある。しかし、含有量が多すぎると、ガラスの粘度が増加し、低温軟化性を損なうので、その含有量は6モル%以下が好ましい。

【0011】 $ZnO$  は、低融性をあまり損なわずに耐水性を向上させるので、 $PbO$ を含まない低融ガラスにとって不可欠な成分である。しかし、含有量が多くなりすぎると、金属との濡れ性を阻害し、ガラスの失透傾向も増加する。また、環境対策の点からも、あまり多すぎる組成は好ましくない。従って、8～22モル%の含有量が適当である。 $BaO$  は、 $ZnO$ と同様の作用効果を有するので、 $ZnO$ との置換に有効な成分である。しかし、 $ZnO$ より低融性や濡れ性を阻害する効果が大きいので、含有量はあまり多くない方が良い。従って、1～12モル%の含有量が適当である。しかも、 $ZnO$ と $BaO$ の合計含有量は、19～24モル%が適当である。

【0012】 $Li_2O$ ,  $Na_2O$  及び  $K_2O$  は、ガラスの溶融性や物性の改善に効果的な成分である。しかし、含有量が多くなりすぎると、低融性は助長されるが、ガラスの耐水性が劣化するので好ましくない。低融性及び耐水性から、 $Li_2O$ と $Na_2O$ については各々7～17モル%の含有量が好ましい。 $K_2O$ は耐水性を劣化させる効果が最も大きいので、0～8モル%の含有量が適

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当である。また、アルカリ金属酸化物は複数種共存させたほうが、混合アルカリ効果により、耐水性の劣化を抑制することができるので、 $Li_2O$ ,  $Na_2O$ 及び $K_2O$ の合計量として25～33モル%の含有量が適当である。

【0013】従って、軟磁性金属、及び、上述のリン酸塩ガラス組成物から軟磁性材料を構成することにより、成形体焼成を低温で行うことができ、作製された成形体の電磁的性質が損なわれることがないうえに、鉛を全く含まず、高い耐水性を備えているので、環境対策の点からも好ましい。更に、成形体焼成温度付近で軟磁性金属とガラス組成物との濡れ性が良いので、より強固で緻密な成形体が得られる。

【0014】そして、請求項1に記載の発明に係る軟磁性材料の特徴構成によれば、軟磁性金属の粉粒体表面を、前記リン酸塩ガラス組成物により被覆しているので、成形体焼成の際、加熱により軟化したガラス組成物は、前記軟磁性金属の粉粒体間に均一に入り込むため、一層上述の効果が増長される。請求項2に記載の発明に係る軟磁性材料の特徴構成によれば、前記軟磁性金属と前記リン酸塩ガラス組成物を混合すれば良いので、簡便に上述の効果を得ることができる。請求項3に記載の発明に係る軟磁性材料の特徴構成によれば、前記軟磁性金属及び前記リン酸塩ガラス組成物を予め焼結成形させていため、最終的に成形体を焼成する際に均一な混合物からなる成形体が得られ、確実に上述の効果を得ることができる。請求項4に記載の発明に係る軟磁性材料の特徴構成によれば、種々の軟磁性金属において、請求項1～3の効果を得ることができ、利便である。

【0015】

【発明の実施の形態】以下に本発明の実施の形態について簡単に説明する。 $Fe_{78}Si_9B_{13}$ （平均粒子径約65μm）の軟磁性金属の粉粒体とリン酸塩ガラス組成物粉粒体（平均粒子径約3μm）を95：5の混合比（体積比）に調合し、以下のように図1に示す粉粒体表面改質装置を用いて、軟磁性金属の粉粒体表面をガラス粉粒体により被覆した複合粉粒体からなる軟磁性材料を作製した。図1は、粉粒体表面改質装置の側部断面図（円筒状容器1の片側端部に近い位置で軸心と直交する方向で切断した図）を示している。密封可能な円筒状容器1の内部に調合した粉粒体9を投入し、回転軸2に固定されたボス3から半径方向に突出する第1アーム4の先端に取付けられた押圧部材5により粉粒体9を押圧・圧縮し、ボス3から第1アームと交叉する半径方向に突出する第2アーム6の先端に取付けられたスクレバー7により粉粒体9を搔き取る操作を、第1アーム4と第2アーム6の回転操作により繰り返して、強力な圧着摩擦力によって、粉粒体間で表面融合を誘発させて、軟磁性金属の粉粒体表面をガラス粉粒体により被覆させた軟磁性材料を作製した。

【0016】次にリン酸塩ガラス組成物の実施例について詳細に説明する。リン酸塩ガラス組成物は、以下のように作製した。炭酸塩（例えば、 $\text{Na}_2\text{CO}_3$ 、 $\text{K}_2\text{CO}_3$ 等）、酸化物（例えば、 $\text{BaO}$ 、 $\text{ZnO}$ 等）、水酸化物（例えば、 $\text{Al(OH)}_3$ 等）及び酸（例えば、 $\text{H}_3\text{PO}_4$ 等）の原料をよく混合した後、高アルミナ質の坩堝を用いて、900°C、1時間、間欠的に攪拌しながら溶融した。その後、融液を予め加熱してあるステンレス板上に流し出し、徐冷して、実質的にモル表示で、 $\text{P}_2\text{O}_5$  39～47%、 $\text{Al}_2\text{O}_3$  3～6%、 $\text{ZnO}$  8～22%、 $\text{BaO}$  1～12%、 $\text{Li}_2\text{O}$  7～17%、 $\text{Na}_2\text{O}$  7～17%、 $\text{K}_2\text{O}$  0～8%、ただし、 $\text{ZnO} + \text{BaO}$  が 19～24%、 $\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$  が 25～33% からなる組成のリン酸塩ガラス組成物を得た。このようにして作製したリン酸塩ガラス組成物のガラス転移点、耐水性、濡れ角を測定した。

【0017】ガラス転移点は、DSC法により、10°C/m in の昇温条件で測定した。この値から、ガラス組成物の低融性がわかる。

【0018】耐水性は、次のようにして求めた値（W）を示す。ガラス組成物 5 g を純水 500 ml 中に 60 分間浸漬させ、引き上げたときの重量（g。）、その後 8 \*

| (数字はモル%)   | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    | 9    |
|--|------|------|------|------|------|------|------|------|------|
| $\text{P}_2\text{O}_5$   | 41.7 | 45.5 | 43.5 | 40.5 | 46.5 | 44.0 | 50.0 | 43.5 | 33.0 |
| $\text{Al}_2\text{O}_3$  | 4.8  | 4.8  | 5.0  | 5.0  | 4.7  | 5.0  | 4.4  | 5.0  | 6.9  |
| $\text{ZnO}$   | 18.6 | 11.1 | 20.5 | 21.5 | 10.8 | 22.0 | 20.0 | 8.5  | 26.7 |
| $\text{BaO}$   | 3.0  | 10.6 | 2.0  | 2.0  | 10.4 |      |      | 14.0 |      |
| $\text{ZnO} + \text{BaO}$  | 21.6 | 21.7 | 22.5 | 23.5 | 21.2 | 21.5 | 20.0 | 22.5 | 26.7 |
| $\text{Li}_2\text{O}$  | 16.0 | 14.0 | 7.5  | 15.5 | 13.7 | 4.0  | 12.8 | 14.5 | 17.2 |
| $\text{Na}_2\text{O}$  | 16.0 | 14.0 | 14.5 | 15.5 | 13.7 | 14.5 | 12.8 | 14.5 | 17.2 |
| $\text{K}_2\text{O}$   |      |      |      |      | 7.0  |      | 10.5 |      |      |
| $\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ | 32.0 | 28.0 | 29.0 | 31.0 | 27.4 | 29.0 | 25.6 | 29.0 | 34.4 |

## 【0022】

※※【表2】

|            | 1                           | 2    | 3    | 4    | 5    | 6    | 7     | 8    | 9    |
|------------|-----------------------------|------|------|------|------|------|-------|------|------|
| $T_g$ (°C) | 303                         | 311  | 307  | 312  | 313  | 315  | 299   | 315  | 330  |
| 耐水性 (%)    | 1.38                        | 1.63 | 1.93 | 1.38 | 1.75 | 4.04 | 36.63 | 1.07 | —    |
| 濡れ角        | $\theta_{450}$              | 92°  | 100° | 84°  | 98°  | 92°  | 129   | 103  | 97   |
|            | $\theta_{540}$              | 18°  | 29°  | 11°  | 28°  | 34°  | 16    | 59   | 103  |
|            | $\theta_{540}/\theta_{450}$ | 0.20 | 0.29 | 0.13 | 0.29 | 0.37 | 0.12  | 0.57 | 1.06 |

※ 結晶析出のため測定不能

【0023】表1、2からわかるように、比較例6～9が、低溶融性、耐水性、濡れ性のうち少なくともひとつの特性に欠けるているのに対して、本発明に係る組成のリン酸塩ガラス組成物は、従来の組成のガラス組成物とは異なり、低溶融性、耐水性、濡れ性のすべてについて優れた特性を備えている。

【0024】〔別実施形態〕以下に他の実施形態を説明する。

(1) 軟磁性金属の粉粒体表面をガラス組成物により被覆する方法は、先の実施形態に限らず、例えば、ゾルゲ

\* 0°Cで24時間乾燥させたときの重量（ $g_\infty$ ）から、次式によりWを求めた。

$$W = (g_0 - g_\infty) / g_\infty \times 100$$

従って、Wの値が小さいほど耐水性が良く、使用上からWは2%以下がほしい。

【0019】次に、濡れ角は以下のようにして測定した。なお、濡れ角とは図2に示すように、液滴の固相一液相界面と液相一気相界面との角度θのことであり、濡れ角θが小さいほど、液体が固体表面をぬらす濡れ性が10高いことを示す。まず、アモルファス金属のリボン上に、ガラス組成物を固めて作成した円筒をのせ、460°Cの炉に入れて30分保持後、濡れ角 $\theta_{450}$ を測定した。その後温度を上げ、同様に、540°Cでの濡れ角 $\theta_{540}$ を測定した。そして、成形体焼成温度付近で軟磁性金属との濡れ性がより良いガラス組成物を得るために $\theta_{450}$ は100°C以下、濡れ角の比 $\theta_{540}/\theta_{450}$ は約0.4以下であるものがほしい。

【0020】表1、2に、リン酸塩ガラス組成物の一例として実施例1～5について、本発明に含まれない組成20のガラス組成物の一例として比較例6～9について、その組成と各特性を示す。

## 【0021】

【表1】

ル法又はプラズマ法等による方法で被覆しても良い。

(2) 軟磁性材料は、先の実施形態に限らず、例えば、ミキサー等により、軟磁性金属とガラス組成物を混合したものでも良い。

(3) 軟磁性材料は、先の実施形態に限らず、軟磁性金属とガラス組成物とを焼結成形したもの、例えば、それらの複合粉粒体や混合物等を焼結成形したものでも良い。

(4) リン酸塩ガラス組成物は先の実施例で説明した成50分に限るものではなく、例えば、 $\text{Al}_2\text{O}_3$  や  $\text{P}_2\text{O}_5$

(5)

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の少量を  $B_2O_3$ ,  $La_2O_3$  及び  $TiO_2$  で置換しても良く、また  $ZnO$  や  $BaO$  の少量を  $SrO$ ,  $CaO$  及び  $MgO$  等で置換しても良い。

(5) 軟磁性金属は、先の実施形態で説明した  $Fe_{18}Si_{12}$  に限るものではなく、例えば、その他の組成比からなる  $Fe-Si-B-M$  ( $M$  は  $Cr$ ,  $W$ ,  $Mo$ ,  $Nb$  から選ばれた少なくとも 1 種の元素) 系非晶質合金、 $Co-Fe-Si-B$  系非晶質合金、 $Fe-Cu-Si-B-M$  ( $M$  は  $Nb$ ,  $W$ ,  $Ta$ ,  $Zr$ ,  $Hf$ ,  $Ti$  及び  $Mo$  から選ばれた少なくとも 1 種の元素) 系等のナノクリスタル、センダスト、各種パーマロイ、 $Fe-Si$  系合金、 $Fe-Ni$  系合金、又は純鉄等であっても良い。

(6) 軟磁性材料におけるリン酸塩ガラス組成物の含有量は、特に限定するものではないが、結合材としての機\*

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\* 能を果たすためには、約 0.5 ~ 20 vol% 程度の含有量が好ましい。

(7) リン酸塩ガラス組成物により軟磁性金属の粉粒体表面を被覆する場合、そのガラス組成物の欠け落ち等により、その厚さが不均一になるのを防ぐため、約  $3 \mu m$  以下の厚さでの被覆が好ましい。

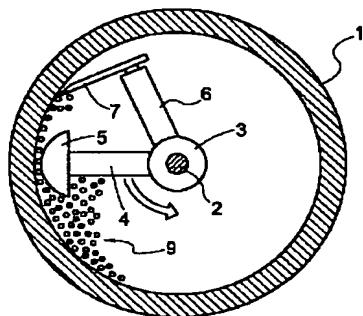
(8) 本発明に係る軟磁性材料を構成するガラス組成物は、不可避の不純物を含んでいても良い。尚、 $SnO$  等の  $Sn$  酸化物を含有する系のガラス組成物は、金属  $Sn$  が析出するため、電気絶縁性等の点で問題があり、 $Sn$  酸化物は含有しない方が良い。

【図面の簡単な説明】

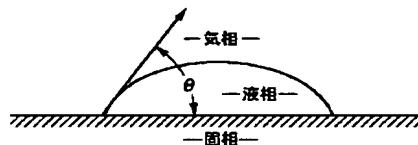
【図 1】 粉粒体表面改質装置の側部断面図

【図 2】 濡れ角の説明図

【図 1】



【図 2】



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HH07 HH09 HH11 HH13 HH15  
HH17 HH20 JJ01 JJ03 JJ05  
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